

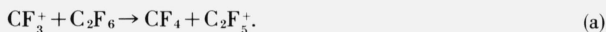
# Reactions of Fluorocarbon Ions in $C_2F_6$ . Implications for the Radiolysis\*

L. W. Sieck, R. Gorden, Jr., and P. Ausloos

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

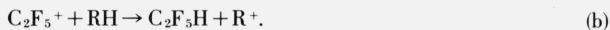
(September 17, 1973)

Reactions of the fragment ions formed in the photoionization of  $C_2F_6$ ,  $Xe-C_2F_6$ , and  $Kr-C_2F_6$  mixtures have been investigated in the NBS photoionization mass spectrometer using both helium (21.2 eV) and neon (16.66–16.84 eV) resonance radiation. Contrary to previously held views, it is shown that  $CF_3^+$  ions having no internal excitation energy undergo the  $F^-$  transfer reaction:



A rate constant of  $4 \pm 1 \times 10^{-11} \text{ cm}^3/\text{molecule} \cdot \text{s}$  is determined for reaction (a) at pressures below  $10^{-2}$  torr. On the basis of the collision rate for these reactants, it can be estimated that, on the average, each  $CF_3^+$  ion undergoes 16 unreactive collisions before undergoing reaction (a). Therefore, from the facts that (1) in pure  $C_2F_6$ , all  $CF_3^+$  ions undergo reaction (a) at high pressures, and (2)  $CF_3^+$  ions formed by charge transfer from  $Xe^+$  ions with a maximum of 8.4 kJ/mol (2 kcal/mol) excess energy undergo reaction (a), one must conclude that reaction (a) is either thermoneutral or exothermic for ground state  $CF_3^+$  ions. Therefore, the earlier estimate for  $\Delta H_f(C_2F_5^+)$  of  $\sim 33$  kJ/mol (8 kcal/mol) must be revised downward:  $\Delta H_f(C_2F_5^+) \leq 3.8$  kJ/mol (0.9 kcal/mol).

The  $C_2F_5^+$  ion is unreactive towards  $C_2F_6$ , but does react with alkanes through the  $H^-$  transfer reaction:



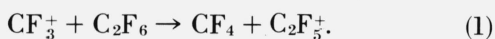
It is suggested that the  $CF_4$  observed in previous gas and liquid phase radiolysis studies of  $C_2F_6$ - $O_2$  mixtures can be entirely ascribed to reaction (a). Small concentrations of impurities or accumulated products will react with the  $C_2F_5^+$  ions under normal low dose rate radiolysis conditions.

Key words: Fluorocarbons; heats of formation; ion-molecule reactions; mass spectrometry; photoionization; rate constants.

## 1. Introduction

The direct and the rare gas-sensitized radiolysis of gaseous and liquid  $C_2F_6$  has been investigated extensively [1].<sup>1</sup> In addition, several mass spectrometric studies have dealt with the reactions of the perfluorinated ions (mainly  $CF_3^+$  and  $C_2F_5^+$ ) formed in  $C_2F_6$  by electron impact [2].

The main reaction channel of the  $CF_3^+$  ion with  $C_2F_6$  is as follows:



From the generally accepted heats of formation of these species [3–4] (for  $C_2F_5^+$  only an estimated heat

of formation was available), it was calculated that reaction (1) was endothermic by at least 29 kJ/mol (7 kcal/mol) [2]. On this basis, the observation of reaction (1) in the ion source of the mass spectrometer has been explained as the reaction of an internally excited  $CF_3^+$  ion. Since this seemed to indicate that the dissociation of the  $C_2F_6^+$  ion resulted in the formation of excited  $CF_3^+$  fragment ions:



the charge exchange reactions of the  $CF_3^+$  ion formed in reaction (2) were investigated in a tandem mass spectrometer [2b]. In these experiments,  $CF_3^+$  ions having an average kinetic energy of 0.3 eV<sup>2</sup>, were

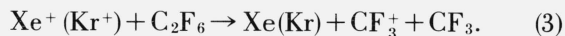
\*Work supported in part by the U.S. Atomic Energy Commission.

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

<sup>2</sup> 1 eV = 96.485 kJ · mol<sup>-1</sup>.

reacted with a variety of compounds having ionization potentials above and below the reported value for  $\text{CF}_3$  (9.17 eV) [3]. The results suggested that some fraction of the  $\text{CF}_3^+$  ions had as much as 2.9 eV internal energy under the conditions of these experiments, since charge exchange was found to occur with  $\text{C}_2\text{H}_4$  (I.P. = 10.5 eV),  $\text{C}_3\text{H}_8$  (I.P. = 11.1 eV), and  $\text{C}_2\text{H}_6$  (I.P. = 11.5 eV) [5]. However, these same charge transfer reactions were not detected in experiments carried out in an ion cyclotron resonance instrument (icr) [2c], and it was concluded that the internally excited  $\text{CF}_3^+$  ions initially produced in reaction (2) had sufficient time to relax during the long time scale of the icr experiment ( $10^{-3}$  s between collisions).

The present study was undertaken with the intention of examining the effect of varying internal energy on the reactions of the  $\text{CF}_3^+$  ion, and to see if reaction (1) can also occur for ground state  $\text{CF}_3^+$  ions. The  $\text{CF}_3^+$  ions were produced by photoionization of  $\text{C}_2\text{F}_6$  using neon (16.66–16.84 eV) and helium (21.2 eV) resonance radiation, and by the charge exchange reaction between  $\text{C}_2\text{F}_6$  and  $\text{Xe}^+$  and  $\text{Kr}^+$  ions:



The reactions of the  $\text{CF}_3^+$  ions formed in these ways were examined in the NBS high pressure photoionization mass spectrometer [5], at a temperature of 300 K. Under these conditions, the ions have no excess kinetic energy.

## 2. Experimental Procedure

All experiments were carried out on the NBS high pressure photoionization mass spectrometer, which has been described in detail previously [5]. The instrument was equipped with the enclosed neon and helium resonance light sources, which deliver photons of 16.66–16.84 eV and 21.2 eV, respectively.

Meaningful experiments could not be carried out at pressures above about 0.5 torr in  $\text{C}_2\text{F}_6$ , because of the appearance of product ions due to reaction with impurities, as well as to a general deterioration of the performance of the quadrupole mass analyzer apparently because of adsorption of  $\text{C}_2\text{F}_6$  on the detector surface. During the early stages of this study, it was found that the mass spectrum obtained from the photoionization of  $\text{C}_2\text{F}_6$  at pressures above approximately 0.1 torr exhibited a number of product ions such as  $\text{CF}_2\text{Cl}^+$  and  $\text{C}_2\text{F}_3\text{Cl}^+$ , which were obviously produced in reactions of  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_5^+$  with chlorinated impurities present in the sample (mainly  $\text{CF}_3\text{Cl}$ ).  $\text{CF}_3\text{Cl}$  has also been reported as an impurity in  $\text{C}_2\text{F}_6$  in several radiolysis investigations [1]. The effects due to this impurity were reduced when the  $\text{C}_2\text{F}_6$  was subjected to gas chromatographic purification, but remaining traces prevented quantitative results from being obtained at  $\text{C}_2\text{F}_6$  pressures above about 0.5 torr. However, for all of the experiments reported here, the total

contribution from impurity ions never exceeded 2 percent of the composite mass spectrum.

## 3. Results and Discussion

### 3.1. Photoionization of Pure $\text{C}_2\text{F}_6$

When  $\text{C}_2\text{F}_6$  was irradiated with 21.2 eV photons, the major primary ions observed at low pressures ( $< 10^{-4}$  torr) were  $\text{CF}_3^+$  (58.5%) and  $\text{C}_2\text{F}_5^+$  (36.8%). Other ions observed were  $\text{CF}^+$ , 3.8 percent, and  $\text{CF}_2^+$ , 0.9 percent. Figure 1 shows the variations in the intensities of the  $\text{CF}_3^+$ ,  $\text{C}_2\text{F}_5^+$ , and  $\text{CF}^+$  ions as the pressure of  $\text{C}_2\text{F}_6$  in the reaction chamber of the mass spectrometer was increased. These results show that reaction (1) does occur under these conditions. That is, the intensity of the  $\text{CF}_3^+$  ion shows a decrease with increasing  $\text{C}_2\text{F}_6$  pressure, and the ionic product of the reaction between  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_6$  must be  $\text{C}_2\text{F}_5^+$  since no other ions show an increase in intensity in this pressure range. From the data obtained at low pressures ( $< 10^{-2}$  torr), an average rate coefficient of  $4 \pm 1 \times 10^{-11}$  cm<sup>3</sup>/molecule-second can be estimated for reaction (1). Within experimental error, the same rate coefficient for this reaction is obtained in experiments in which ionization of  $\text{C}_2\text{F}_6$  is effected by 16.66–16.84 eV photons; (in that case, only  $\text{CF}_3^+$ , 39% and  $\text{C}_2\text{F}_5^+$ , 61%, ions are observed in the system at the "zero" pressure limit). It is important to note that this estimate of the rate coefficient for reaction (1) is based on a slope of a decay curve for  $\text{CF}_3^+$  which represents the reaction of only 5 percent of these ions. Nevertheless, this value agrees within the

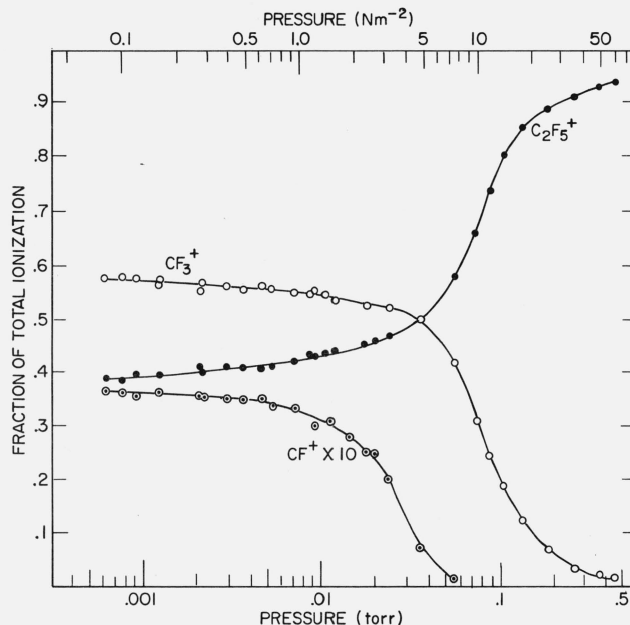


FIGURE 1. Photoionization of  $\text{C}_2\text{F}_6$  at 58.4 nm (21.2 eV).

Fractional intensities of  $\text{CF}^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_5^+$  as a function of pressure.

experimental limits with the value of  $3.4 \times 10^{-11}$  cm<sup>3</sup>/molecule-second reported earlier [2b].

Because the residence time of the ions in the mass spectrometer is not precisely known at pressures above  $10^{-2}$  torr, reliable rate coefficient estimates can not be obtained from the data taken in the higher pressure ranges. These results are, however, of interest, since they show that at pressures around 0.5 torr, essentially all of the  $\text{CF}_3^+$  ions have reacted to form  $\text{C}_2\text{F}_5^+$  (the fact that the ion currents shown in the figure do not add up to 100 percent in the high pressure region is to be explained by the impurity effects described in the Experimental Section). This observation is in general agreement with the results obtained by Marcotte and Tiernan [2b] in a time-of-flight mass spectrometer, which showed that at a pressure of  $\sim 0.4$  torr, about 50 percent of the  $\text{CF}_3^+$  ions had reacted with  $\text{C}_2\text{F}_6$ . Since the observed rate constant for reaction (1) is about  $4 \times 10^{-11}$  cm<sup>3</sup>/molecule-second, and the rate constant for collisions between such fluorocarbon ions and  $\text{C}_2\text{F}_6$  is on the order of  $7 \times 10^{-10}$  cm<sup>3</sup>/molecule-second [6-7], a  $\text{CF}_3^+$  ion undergoes  $\sim 16$  unreactive collisions with  $\text{C}_2\text{F}_6$  on the average before reacting. This means that if only  $\text{CF}_3^+$  ions having excess internal energy could undergo reaction (1), one would expect to observe a decrease in the rate of reaction (1) as collisional deactivation becomes more important at higher pressures. The fact that all  $\text{CF}_3^+$  ions eventually react in our system is inconsistent with this interpretation.

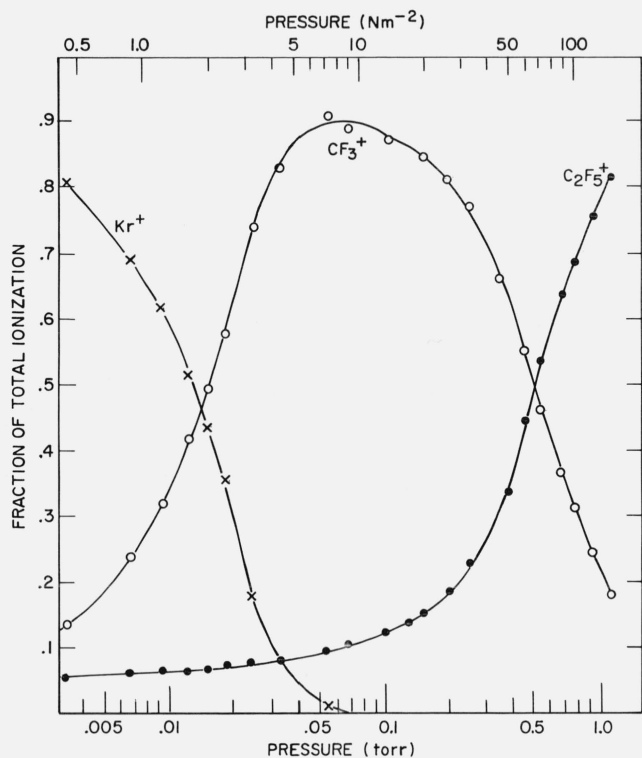


FIGURE 2. Photoionization of  $\text{Kr-C}_2\text{F}_6$  (1:0.08) mixture at 74.4-73.6 nm (16.67-16.84 eV).

Fractional intensities of  $\text{Kr}^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_5^+$  as a function of pressure.

The results given in Figure 1 also confirm the observation made previously [2] that the  $\text{C}_2\text{F}_5^+$  ions produced either as primary fragments or as reaction products do not react further with  $\text{C}_2\text{F}_6$ .

The results obtained in the 21.2 eV photoionization experiments also lead to estimates of the values of the rate coefficients for the reactions of the  $\text{CF}^+$  and  $\text{CF}_2^+$  ions with  $\text{C}_2\text{F}_6$  of  $1.9 \pm 0.4 \times 10^{-10}$  cm<sup>3</sup>/molecule-second and  $1.45 \pm 0.30 \times 10^{-9}$  cm<sup>3</sup>/molecule-second, respectively.

### 3.2. Photoionization of $\text{C}_2\text{F}_6$ -Rare Gas Mixtures

Figures 2 and 3 show the results of experiments in which krypton or xenon was irradiated with 16.66-16.84 eV photons in the presence of small amounts (8.2 %) of added  $\text{C}_2\text{F}_6$ . In such experiments, most of the initial ionization is effected in the rare gas, which, upon collision with  $\text{C}_2\text{F}_6$  molecules, transfers charge (if charge transfer is exothermic) according to reaction (3). The energies available from the recombination energies of the rare gas ions are 14.0 and 14.7 eV in the case of  $\text{Kr}^+$ , and 12.13 or 13.44 eV in the case of  $\text{Xe}^+$  [5]. Therefore, charge transfer from these ions to  $\text{C}_2\text{F}_6$  should not result in the formation of  $\text{C}_2\text{F}_5^+$  fragment ions since there is insufficient energy available (the observed appearance potential of  $\text{C}_2\text{F}_5^+$  from  $\text{C}_2\text{F}_6$  is about 15.4 eV) [7]. Actually, in the case of  $\text{Kr}^+$  ions,

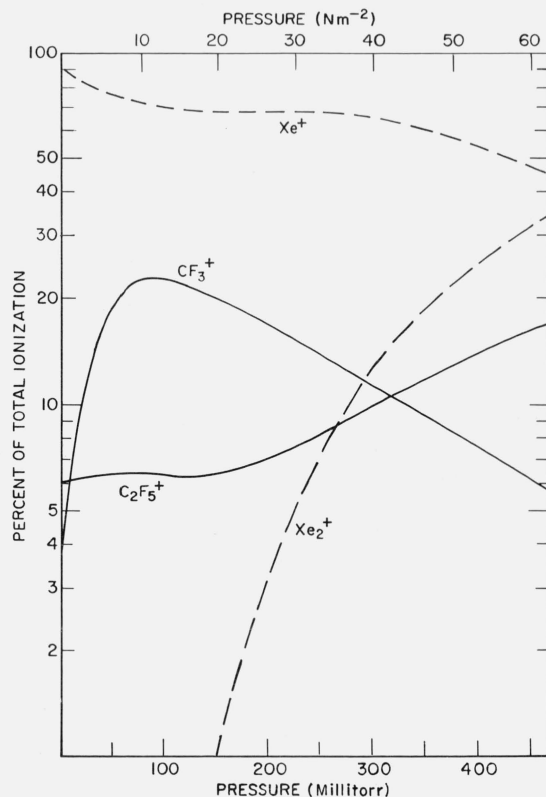


FIGURE 3. Photoionization of  $\text{Xe-C}_2\text{F}_6$  (1:0.08) mixture at 74.4-73.6 nm (16.67-16.84 eV).

Fractional intensities of  $\text{Xe}^+$ ,  $\text{Xe}_2^+$ ,  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_5^+$  as a function of pressure.

reported charge transfer spectra of  $C_2F_6$  confirm that process (3) accounts for 93–98 percent of the  $Kr^+ \cdot C_2F_6$  reactive encounters. In the case of xenon ions, only those ions produced in the  $^2P_{1/2}$  state (13.44 eV) have sufficient energy to undergo reaction (3), while the ground state  $^2P_{3/2}$   $Xe^+$  ions (12.13 eV) will be unreactive with  $C_2F_6$ .

The results presented in figure 2 show that the intensity of the  $Kr^+$  ion diminishes as that of  $CF_3^+$  increases because of the occurrence of reaction (3) as the pressure is increased in the  $Kr \cdot C_2F_6$  mixture. At pressures above 0.05 torr, reaction of the  $CF_3^+$  ion to form  $C_2F_5^+$  is observed. At the low pressure limit, where charge exchange does not occur to any appreciable extent, some  $C_2F_5^+$  is produced by direct photoionization of  $C_2F_6$ .

More interesting conclusions can be derived from the results given in figure 3 which shows the data obtained in the xenon- $C_2F_6$  mixture irradiated with 16.67–16.84 eV photons in the photoionization mass spectrometer. Here the  $Xe^+(^2P_{1/2})$  ions (apparently about 30% of the  $Xe^+$  ions formed under these conditions) undergo reaction (3) to produce  $CF_3^+$  ions in  $C_2F_6$ . The interesting point here is that if one accepts a heat of formation of  $CF_3^+$  of 414 kJ/mol (99.1 kcal/mol) [3], then the  $CF_3^+$  ions formed in reaction (3) involving  $Xe^+(^2P_{1/2})$  and  $C_2F_6$  can only have a *maximum* of 8.4 kJ/mol (2 kcal/mol) excitation energy. Even so, these  $CF_3^+$  ions undergo reaction (1) to form  $C_2F_5^+$  product ions (fig. 3). Since it is to be expected that an endothermic reaction would proceed at a rate which would not be observable under these experimental conditions, we are forced to conclude that if the overall sequence (reaction (3) followed by reaction (1)):



is thermoneutral, then the heat of formation of  $C_2F_5^+$  can not be greater than 12 kJ/mol (2.9 kcal/mol). If we accept, as is probably the case, that the  $CF_3^+$  ions have no internal energy at the time of reaction (1), a value for  $\Delta H_f(C_2F_5^+)$  of 4 kJ/mol (0.9 kcal/mol) is obtained. Thus we must conclude that the value of 34 kJ/mol (8.1 kcal/mol) calculated earlier [1b] for  $\Delta H_f(C_2F_5^+)$  is too high, and reaction (1) has therefore erroneously been assumed to be an endothermic reaction.

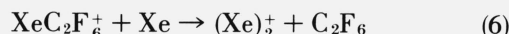
Figure 3 also shows that there is a slight increase in the yield of  $C_2F_5^+$  at pressures below about 0.1 torr, where reaction (1) can not be important. It is likely that this observation is an experimental artifact caused by slight changes in the composition of the xenon- $C_2F_6$  mixture due to fractionation at the automatic leak assembly. However, the possibility can not be excluded that a reaction occurs between  $Xe^+(^2P_{1/2})$  and  $C_2F_6$  to form  $C_2F_5^+$ :



Accepting an estimate of the Xe-F bond strength of

$134 \pm 17$  kJ/mol ( $32 \pm 4$  kcal/mol) [8], one obtains an estimate for  $\Delta H_f(XeF)$  of  $-54 \pm 17$  kJ/mol ( $-13 \pm 4$  kcal/mol) and on this basis, reaction (5) may be slightly exothermic. In this connection, it should be pointed out that when Marcotte and Tiernan [2b] impacted  $Xe^+$  ions onto  $C_2F_6$  in a tandem mass spectrometer, they observed  $C_2F_5^+$  as the major product ion (79%) even though, as discussed above, charge transfer from  $Xe^+$  ions to yield this fragment is strongly endothermic. This unusual result could perhaps be explained by the occurrence of a reaction such as (5), which might be favored for ions which are translationally heated. On the other hand, it should be mentioned that in experiments carried out in this laboratory in an icr instrument, there was no evidence for the production of  $C_2F_5^+$  ions through a reaction of  $Xe^+$  with  $C_2F_6$ .

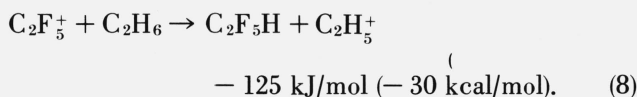
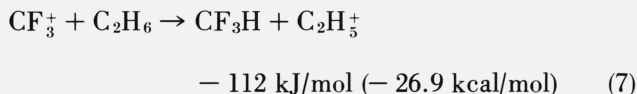
A final point to be mentioned in connection with the results given in figure 3 is the formation of  $Xe_2^+$  as a product ion in a pressure region in which this ion would not be observed in pure xenon. This can be explained by the occurrence of a switching reaction involving the  $XeC_2F_6^+$  association ion and xenon atoms:



Apparently the  $XeC_2F_6^+$  is not detected in our experiments due to the fact that the dissociative lifetime of  $XeC_2F_6^+$  is much shorter than the total ion transit time in our instrument.

### 3.3. Photoionization of $C_2F_6$ -Alkane Mixtures

In view of the fact that the photoionization curves of  $C_2F_5^+$  and  $CF_3^+$  indicate that these species probably do contain excess energy when formed by fragmentation of  $C_2F_6^+$  [7], and because these species have been reported, under certain conditions [2b] to undergo charge transfer with molecules such as ethane and propane, with which charge transfer involving ground state ions would be endothermic, it was considered worthwhile to add ethane to  $C_2F_6$  irradiated with 16.66–16.84 eV photons. The results of such experiments, in which  $C_2F_6$  containing 5 percent ethane was irradiated at various pressures with 16.66–16.84 eV photons are given in figure 4. It is seen that there is no evidence for charge transfer reactions from  $CF_3^+$  or  $C_2F_5^+$  to  $C_2H_6$ . However, both these fluorinated ions undergo exothermic hydride transfer reactions with ethane:



Small amounts of  $C_2H_4^+$  and  $C_2H_6^+$  are observed, and can be attributed to direct photoionization of the

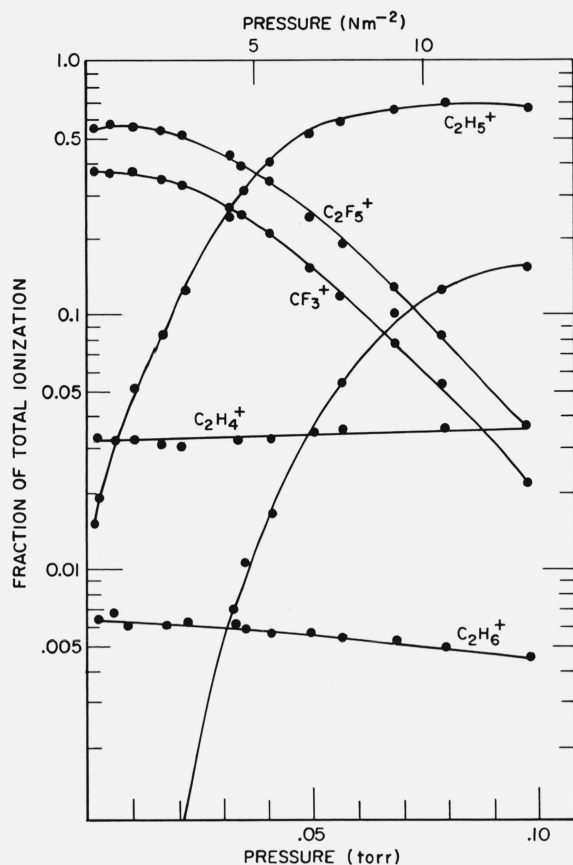
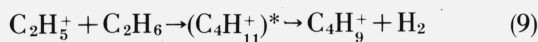


FIGURE 4. Photoionization of  $C_2F_6$ - $C_2H_6$  (1:0.05) mixture at 74.4–73.6 nm (16.67–16.84 eV).

Fractional intensities of  $C_2H_4^+$ ,  $C_2H_5^+$ ,  $C_2H_6^+$ ,  $C_4H_9^+$ ,  $CF_3^+$ , and  $C_2F_5^+$  as a function of pressure.

ethane additive. At pressures above about 0.03 torr, the  $C_4H_9^+$  product ion is formed through the occurrence of the well-known reaction sequence:

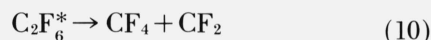


Addition of higher alkanes,  $C_3H_8$  (I.P. 11.1 eV) and  $n$ - $C_4H_{10}$  (I.P. 10.6 eV) indicates that in these cases  $H^-$  transfer to  $CF_3^+$  and  $C_2F_5^+$  is also the only reaction mode. It should be noted that because we are dealing here with dilute  $C_2F_6$ -alkane mixtures the  $CF_3^+$  and  $C_2F_5^+$  ions will probably be collisionally deactivated at the time of reaction with the alkane molecule.

### 3.4. Implications for Radiolysis

In the 70 eV mass spectrum,  $CF_3^+$  and  $C_2F_5^+$  account for 48 percent and 25.5 percent of the cations, respectively. The parent ion is absent, as is the case for many halocarbons. Since the parent ion apparently has a short lifetime, and it may therefore be anticipated that fragmentation will still be important at the pressures encountered in radiolysis experiments. However, the relative abundances of the various fragment ions can not be predicted with certainty, since these will depend on the density of the system. It can, however, be surmised that the major ion in the mass spectrum,  $CF_3^+$ , will be present in the gas phase radiolysis of  $C_2F_6$  and possibly even in the liquid phase radiolysis.

In some of the experiments performed during the course of this study in the photoionization mass spectrometer, up to 10 percent oxygen was added to  $C_2F_6$  and no interactions between  $O_2$  and the fluorocarbon ions were observed. Thus, it is of interest that radiolysis experiments carried out on  $C_2F_6$  in the presence of 1 mol percent oxygen, at a pressure of two atmospheres [1a], show the formation of  $CF_4$  as a product with a  $G$  value of 1.3 [ $M/N_+ = 0.46$  since  $W(C_2F_6) = 35.8$  eV. (table 1)] In the same study [1a], the yields of  $C_3F_8$  and  $C_4F_{10}$  are reduced to zero when oxygen is added, indicating that the fluorocarbon radicals are effectively scavenged by oxygen. Therefore, reaction of  $CF_3$  can not contribute to the formation of  $CF_4$  in the presence of oxygen. These results indicate that the formation of  $CF_4$  in this experiment can be attributed to reaction (1), and therefore, that ionization of  $C_2F_6$  at a pressure of two atmospheres leads to the formation of  $CF_3^+$  fragment ions with an ion pair yield of approximately 0.46. It may also be mentioned that an alternate channel for formation of  $CF_4$  which has been mentioned, namely the decomposition of excited  $C_2F_6$



can be excluded since the formation of this product is inhibited by the addition of bromine to the system [1g]. There is no reason to expect that small concentrations of bromine would have any effect on the primary decomposition of an electronically excited molecule.

Similar conclusions can be reached in the radiolysis of  $C_2F_6$  in the liquid phase [1d] (table 1). That is, the addition of 10 percent oxygen inhibits the formation of  $C_3F_8$  and  $C_4F_{10}$ , but  $CF_4$  is formed in the presence of

TABLE 1. Product yields per 100 eV ( $G$ ) in  $C_2F_6$  Radiolysis

Conditions	$G(CF_4)$	$G(C_3F_8)$	$G(n-C_4F_{10})$	Other	Reference
Gas, 2 atm (200 kNm <sup>-2</sup> ).....	2.5	0.45	0.20		[1a].
Gas, 2 atm (200 kNm <sup>-2</sup> ) + 1% $O_2$ .....	1.3	0.0	0.0		[1a].
Gas, (7–500 kNm <sup>-2</sup> ) + $Br_2$ .....	undetectable	0.0	0.0	$G(CF_3Br) = 2.70 \pm 0.3$ $G(C_2F_5Br) = 3.00 \pm 0.3$	[1g]. [1g].
Liquid.....	1.72	0.87	0.45		[1d].
Liquid + ~ 10% $O_2$ .....	0.97	0.0	0.0		[1d].

oxygen with a  $G$  value of approximately unity. Thus, as in the gas phase, evidence points to the formation of  $\text{CF}_4$  through reaction (1). We can tentatively conclude, therefore, that ionic fragmentation to form  $\text{CF}_3^+$  does occur in the liquid phase radiolysis of  $\text{C}_2\text{F}_6$ .

As pointed out earlier in the discussion, reaction (1) is a slow reaction. This means that if any other reactive compound is present in the system—as an impurity, an additive, or as an accumulated product—the  $\text{CF}_3^+$  ions may be intercepted by the foreign compound before reacting with  $\text{C}_2\text{F}_6$ . Consequently, one would expect the yield of  $\text{CF}_4$  to be sensitively affected by the presence of foreign compounds in the system. The reduction of the yield of  $\text{CF}_4$  in the radiolysis of  $\text{C}_2\text{F}_6$  when bromine is added illustrates this point [1g]. The results presented in that study showed that a small concentration of  $\text{CF}_3\text{Cl}$  impurity affected the ion-molecule kinetics of the system strongly, especially with respect to the fate of the unreactive  $\text{C}_2\text{F}_5^+$  ion.

We do not at present have any information concerning the ionic reactions which occur when bromine, chlorine, or  $\text{HCl}$  are added to  $\text{C}_2\text{F}_6$ , as they were in a recent radiolysis study [1g]. It is of interest, however, that in that study  $\text{CF}_3\text{Cl}$  was found as a product in the radiolysis of  $\text{C}_2\text{F}_6\text{-HCl}$  mixtures, while  $\text{CF}_3$  radicals are known to react with  $\text{HCl}$  to give  $\text{CF}_3\text{H}$ , exclusively [9]. As pointed out by the authors of that study, this may be considered as evidence of a contribution from ionic processes.

The authors would like to thank Drs. John Eyler and Sharon Lias for performing several confirmatory experiments in relation to this study using an ion cyclotron resonance instrument. They would also like to thank

Dr. Lias for her help in the preparation of the final version of the manuscript and Dr. Eugene Domalski of the Thermochemistry Section for providing essential thermodynamic information pertinent to this study.

#### 4. References

- [1a] Kevan, L., and Hamlet, P., *J. Chem. Phys.* **42**, 2255 (1965).
- [b] Kevan, L., *Ibid.* **44**, 683 (1966).
- [c] Fessenden, R. W., and Schuler, R. H., *Ibid.* **43**, 2704 (1965).
- [d] Sokolowska, A., and Kevan, L., *J. Phys. Chem.* **71**, 2220 (1967).
- [e] Sokolowska, A., and Kevan, L., *Ibid.* **72**, 253 (1968).
- [f] Askew, W. C., Reed, T. M., and Mailen, J. C., *Radiat. Res.* **33**, 282 (1968).
- [g] Cooper, R., and Haysom, H. R., *J. Chem. Soc. Faraday Trans. II*, **69**, 904 (1973).
- [2a] King, J., Jr., and Ellemann, D. D., *J. Chem. Phys.* **48**, 412 (1968).
- [b] Marcotte, R. E., and Tiernan, T. O., *Ibid.* **54**, 3385 (1971).
- [c] Su, T., and Kevan, L., *J. Phys. Chem.* **77**, 148 (1973).
- [3] Walter, T. A., Lifshitz, C., Chupka, W. A., and Berkowitz, J., *J. Chem. Phys.* **51**, 3531 (1969).
- [4a] JANAF Thermochemical Tables. Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37 (June 1971).
- [b] Franklin, J. L., Dillard, J. G., Rosenstock, H. M., Herron, J. T., Draxl, K., and Field, F. H., *Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions*. Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), NSRDS-26, 289 pages (1969).
- [5a] Sieck, L. W., Searles, S. K., and Ausloos, P., *J. Amer. Chem. Soc.* **91**, 7627 (1969).
- [b] Sieck, L. W., Gorden, R., Jr., Ausloos, P., Lias, S. G., and Field, F., *Radiat. Res.* (in press).
- [6] Kevan, L., and Futrell, J. H., *J. Chem. Soc. Faraday Trans. II*, No. 5, 2 (1972).
- [7] Noutary, C. J., *J. Res. Nat. Bur. Stand. (U.S.)*, 72A (Phys. and Chem.), 479-485 (Sept.-Oct. 1968).
- [8] Johnson, G. K., Malm, J. G., and Hubbard, W. N., *J. Chem. Thermodynamics* **4**, 879 (1972).
- [9] Amphlett, J. C., and Whittle, E., *Trans. Faraday Soc.* **61**, 484 (1965).

(Paper 78A2-809)